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Mechanisms of Acid-Catalyzed Aliphatic Ketone Rearrangements and Relationships between Ketone Structure and Oxygen Function Rearrangement. Tracer Studies on 3-Methyl-2-butanone-*1*-^{14}C, 3-Methyl-2-butanone-*2*-^{14}C, 3,3-Dimethyl-2-butanone-*2*-^{14}C, and 2,4-Dimethyl-3-pentanone-*3*-^{13}C[1]

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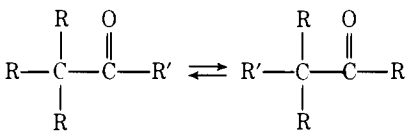
Abstract: Systematic carbon-14 and carbon-13 tracer studies and other evidence have shown that α-disubstituted ketones undergo acid-catalyzed rearrangements to isomeric ketones via a series of alkyl and oxygen function shifts in ketone conjugate acids and tertiary carbenium ions derived from them. Rearrangements via alkyl shifts only are faster than oxygen function rearrangements. Thus, the major product from the rearrangement of 2,2,4-trimethyl-3-pentanone-*3*-^{13}C (**10a**) is 3,3,4-trimethyl-2-pentanone-*2*-^{13}C (**11a**), but smaller amounts of oxygen function rearrangement product 3,3,4-trimethyl-2-pentanone-*3*-^{13}C (**11b**) are also formed; slow oxygen function rearrangement accompanies more rapid methyl scrambling in 3,3-dimethyl-2-butanone-*1*-^{14}C (**5c**) and -*2*-^{14}C (**5a**). For α-monosubstituted ketones acid-catalyzed alkyl group interchange takes place but no oxygen function rearrangement is observed, demonstrating that the reaction path involves tertiary carbenium ions and aldehyde conjugate acids, but not secondary carbenium ions. Thus, alkyl-group interchanges but no oxygen-function rearrangements were observed in the rearrangements of 3-methyl-2-butanone-*1*-^{14}C (**2c**) and -*2*-^{14}C (**2a**); the conversion of 2,4-dimethyl-3-pentanone-*3*-^{14}C (**8a**) to 3,4-dimethyl-2-pentanone-*2*-^{14}C (**9a**) takes place without the formation of 2,4-dimethyl-3-pentanone-*3*-^{14}C (**9b**). α-Unsubstituted ketones, which undergo acid-catalyzed rearrangements only with great difficulty, appear to do so with complete oxygen function rearrangement. Concerted epoxide conjugate acid formation and decomposition are suggested as the mechanism for these reactions. Two different catalyst systems, homogeneous reaction in concentrated sulfuric acid and heterogeneous reaction by passage of the ketone vapor over solid supported phosphoric acid, do not exhibit any qualitative differences in their abilities to promote the ketone rearrangements or the oxygen function rearrangements. Generalized mechanisms for the three different types of substrates are given.

Introduction

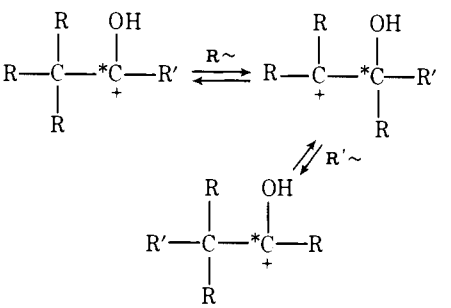
A substantial number of acid-catalyzed rearrangements of aldehydes and ketones to isomeric carbonyl compounds are reported in the literature, and the scope and mechanisms of the reactions were reviewed by Fry[3] in 1971 and Collins and Eastham[4] in 1966. Generally, these reactions involve interchange of a group attached directly to the carbonyl carbon on one side with a group attached to the α carbon on the other side, eq 1.



R and R' = H, alkyl, or aryl (1)

The simplest mechanistic path for these reactions, mechanism Ia, eq 2, involves conventional 1,2-hydrogen and/or alkyl shifts in the ketone conjugate acids or aldehyde conjugate acids and carbenium ions derived from them[5,6] (for comparisons to later mechanisms these formulations assume the use of car-

mechanism Ia



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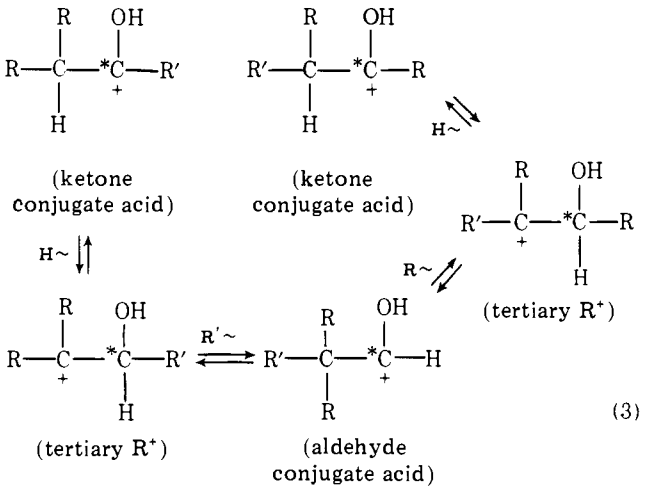
bon-13 or carbon-14 labeled reactants). In cases where the intermediate carbenium ion in mechanism Ia would be secondary or primary, an alternate series of hydrogen and alkyl shifts, mechanism Ib, eq 3, involving the intermediacy of the

mechanism Ib

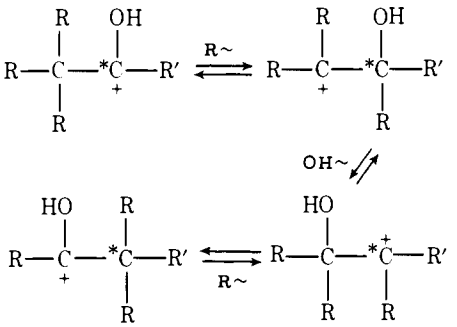


(3)

more stable tertiary carbenium ions and an aldehyde conjugate acid is favored.[7]

The same chemical results can be obtained from a substantially different set of mechanisms[8] involving oxygen function rearrangement[9] coupled with hydrogen and/or alkyl shifts, mechanism IIa, eq 4. Generally, these rearrangement

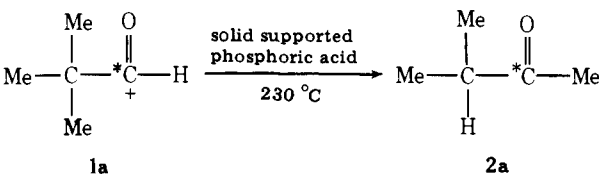
mechanism IIa



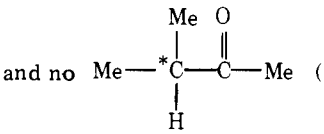
(4)

paths can only be detected by carbon tracer studies (compare eq 2 and 4). Other oxygen function rearrangement mechanisms[3,10,11] involve transfer of the oxygen function in a stepwise or concerted fashion from one carbon to another through an epoxide or an epoxide conjugate acid, by reversible pinacol formation, and by reversible alkyne formation.

A main purpose of the present research was to attempt to determine which structural features permit and which prevent oxygen function rearrangement in the acid-catalyzed rearrangements of aliphatic ketones.[12] At the inception of this research the following rather puzzling set of results had accumulated. When passed over solid supported phosphoric acid at 230 °C, trimethylacetaldehyde-*1*-^{14}C (**1a**) rearranges[13] without oxygen function rearrangement to 3-methyl-2-butanone-*2*-^{14}C (**2a**), with no 3-methyl-2-butanone-*3*-^{14}C (**2b**), eq 5. Further treatment of α-monosubstituted ketone **2a** with this catalyst at 230 °C gave none of oxygen function rearrangement product, **2b**. However, both α-unsubstituted and α-disubstituted ketones give oxygen function rearrangements. 3-Pentanone-*3*-^{14}C (**3a**), upon passage over solid supported phosphoric acid, gave[14] 99% of oxygen function rearranged product 2-pentanone-*3*-^{14}C (**4b**) and only 1% of 2-pentanone-*2*-^{14}C (**4a**), eq 6. Upon treatment with concentrated sulfuric acid, 3,3-dimethyl-2-butanone-*2*-^{14}C (**5a**) does rearrange slowly[11] to oxygen function rearrangement product 3,3-dimethyl-2-butanone-*3*-^{14}C (**5b**), eq 7.

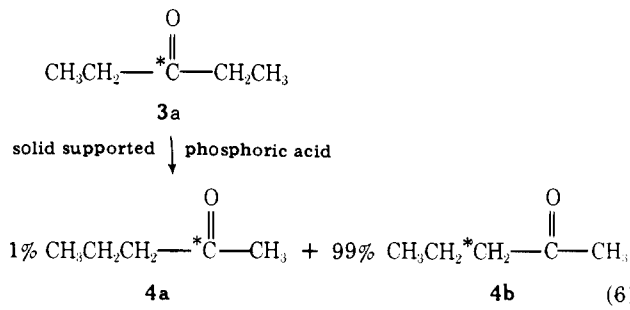


1a **2a**

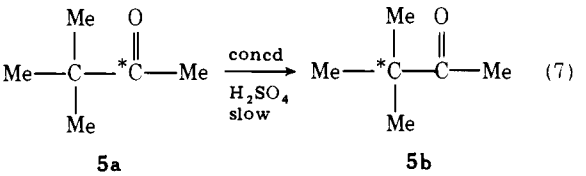


(5)

2b



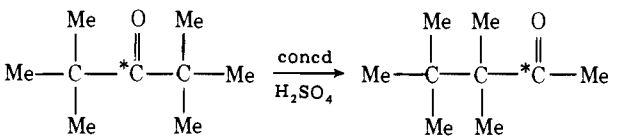
3a **4a** **4b** (6)



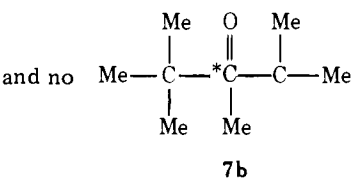
(7)

5a **5b**

Another α-disubstituted ketone, 2,2,4,4-tetramethyl-3-pentanone-*3*-^{14}C (**6a**), was reported[15] to rearrange to 3,3,4,4-tetramethyl-2-pentanone-*2*-^{14}C (**7a**) without oxygen function rearrangement, eq 8. In this work of Barton and



6a **7a**



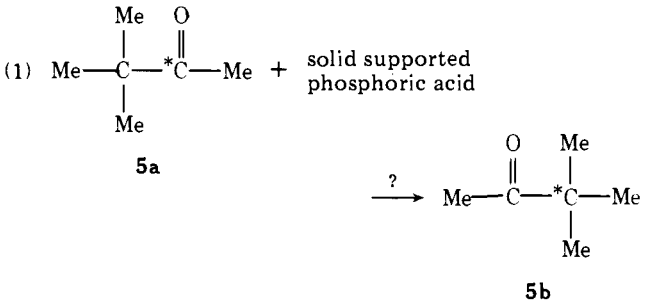
(8)

7b

Porter[15] the primary conclusion concerning the major path of the reaction must be correct, but there is not a good carbon-14 activity balance in their work between a degradation product and its precursor (a difference of about 10%), so it is questionable as to whether a minor oxygen function rearrangement path can be ruled out. Furthermore, in this case, under the reaction conditions the product 3,3,4,4-tetramethyl-2-pentanone undergoes a cleavage reaction to isobutene and 3-methyl-2-butanone, and this may prevent the long-term exposure needed to determine whether there is a minor oxygen function rearrangement reaction path.

Two quite different acid catalysts, solid supported phosphoric acid and concentrated sulfuric acid, had been used in these experiments and it seemed important to find out whether this was the cause for some of the differences noted. On the basis of a mechanistic analysis (the details will be developed

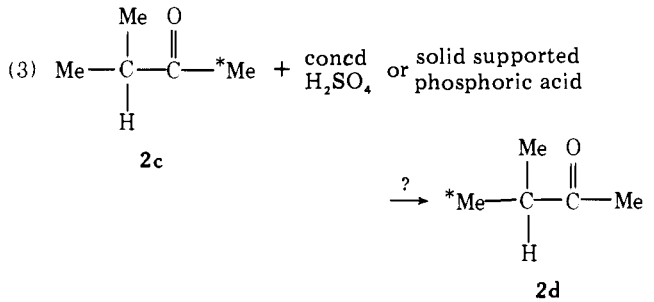
Chart I



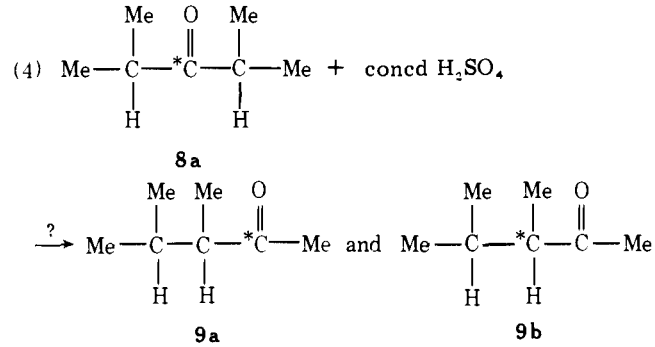
prediction: **5b** will be formed (slow oxygen function rearrangement)

(2) **2a** + concd H_2SO_4 or solid supported phosphoric acid under drastic conditions $\xrightarrow{?}$ **2b**

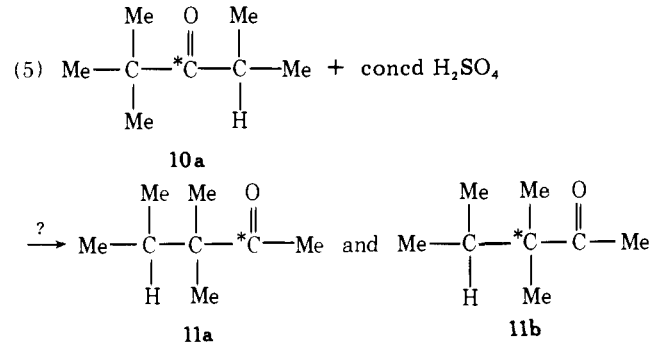
prediction: no **2b** will be formed with either catalyst (no oxygen function rearrangement)



prediction: **2d** will be formed with both catalysts



prediction: **9a** will be formed but oxygen function rearrangement product **9b** will not



prediction: **11a** will form as the major product together with smaller amounts of **11b** (slow oxygen function rearrangement)

Table I. Activity Results (mCi/mol) Obtained by Repeated Passage of 3,3-Dimethyl-2-butanone-*2*-^{14}C[a] (**5a**) over Solid Supported Phosphoric Acid Catalyst at 225 °C

catalyst passes	acetanilide	*tert*-butyl 3,5-dinitrobenzoate
0[b]	0.0574 ± 0.0004	0.0002 ± 0.0000
1	0.0562 ± 0.0002	0.0021 ± 0.0001
3	0.0536 ± 0.0002	0.0049 ± 0.0001
5	0.0516 ± 0.0004	0.0065 ± 0.0001
6	0.0500 ± 0.0001	0.0085 ± 0.0001

[a] The radioactivity of the starting ketone was 0.0578 ± 0.0004 mCi/mol. [b] Starting material isotopic purity and degradation procedure check.

in the Discussion section of this paper), it was predicted that the nature of the catalyst would not cause major differences, that α-unsubstituted ketones would rearrange with nearly exclusive oxygen function rearrangement, that α-monosubstituted ketones would rearrange without oxygen function rearrangement, and that a relatively rapid rearrangement of α-disubstituted ketones to isomeric ketones would be accompanied by slow oxygen function rearrangement. These predictions were tested by the tracer experiments shown in Chart I.

Experiment 5 was carried out using carbon-13 tracer techniques, and the results, which are reported elsewhere,[16] will be summarized in the Discussion section of this paper. Experiments 1–4 were carried out using carbon-14 tracer techniques as described below.

Results and Discussion

Rearrangement of 3,3-Dimethyl-2-butanone-*2*-^{14}C (5a) on Solid Supported Phosphoric Acid. 3,3-Dimethyl-2-butanone is known to undergo both relatively fast methyl scrambling[18] (3,3-dimethyl-2-butanone-*1*-^{14}C (**5c**) and 3,3-dimethyl-2-butanone-*4*-^{14}C (**5d**) interconvert) and slower oxygen function rearrangement,[11] **5a** → **5b**, in concentrated sulfuric acid. In order to investigate the possibility that important differences in rearrangement behavior might be caused by differences between the homogeneous sulfuric acid catalyst and the heterogeneous solid supported phosphoric acid catalyst, the conversion of **5a** to **5b** on this catalyst was investigated. The experimental procedures for the preparation of the labeled ketone, the rearrangement, and the degradation of the recovered ketone have been described.[11,13] The degradation of the product 3,3-dimethyl-2-butanone-*X*-^{14}C involved peracid oxidation to *tert*-butyl acetate, followed by derivatization of the acid and alcohol components of the ester to acetanilide and *tert*-butyl 3,5-dinitrobenzoate, respectively. Thus, the activities of the acetanilide and *tert*-butyl 3,5-dinitrobenzoate are measures of the amounts of the label in the acetyl and *tert*-butyl groups of the ketone. The results are shown in Table I.

The "zero passes" data show the isotopic purity of the starting material and the adequacy of the degradation procedure. The activity balances in all cases are good. The results clearly show that oxygen function rearrangement does take place, as predicted, and thus that there is no qualitative difference in catalytic behavior between the concentrated sulfuric acid and solid supported phosphoric acid catalyst systems.

Rearrangement of 3-Methyl-2-butanone-*2*-^{14}C (2a) and 3-Methyl-2-butanone-*1*-^{14}C (2c). Following the finding[13] that **2a** did not undergo oxygen function rearrangement with solid supported phosphoric acid catalyst at 230 °C, further experiments were carried out with this catalyst at 290 °C and with concentrated sulfuric acid at 100 °C. In both cases, conditions were arranged to be as drastic as possible while still permitting recovery of useful amounts of product. In both cases there was

Table II. Activity Results (mCi/mol) from Rearrangement Experiments with 3-Methyl-2-butanone-2-^{14}C (**2a**) on Solid Supported Phosphoric Acid Catalyst[a] at 290 °C and in Concentrated Sulfuric Acid[b] at 100 °C

conditions	acetanilide	isopropyl 3,5-dinitrobenzoate
H_2SO_4, 0 time sample[c]	not determined	0.0002[d] + 0.0000
H_2SO_4, 2 h	0.0840 ± 0.0005	0.0002[d] ± 0.0000
H_2SO_4, 3 h	0.0840 ± 0.0004	0.0001[d] ± 0.0000
H_3PO_4 catalyst, 1 pass	0.113[e]	0.0006 ± 0.0001
H_3PO_4 catalyst, 3 passes	0.113 ± 0.001	0.0016 ± 0.0001
H_3PO_4 catalyst, 4 passes	0.114 ± 0.001	0.0021 ± 0.0001

[a] The radioactivity of the starting ketone was 0.114 ± 0.001 mCi/mol. [b] The radioactivity of the starting ketone was 0.0844 ± 0.0004 mCi/mol. [c] Starting material isotopic purity and degradation procedure check. [d] Indistinguishable from the counting rate for blank samples. [e] Single result.

Table III. Activity Results (mCi/mol) from Rearrangement Experiments with 3-Methyl-2-butanone-1-^{14}C (**2c**) on Solid Supported Phosphoric Acid Catalyst[a] at 225 °C, and in Concentrated Sulfuric Acid[b] at 100 °C

conditions	acetanilide	isopropyl 3,5-dinitrobenzoate
H_2SO_4, 0 time sample[c]	0.249 ± 0.002	0.0006 ± 0.0001
H_2SO_4, 2 h	0.184 ± 0.001	0.066 ± 0.000
H_2SO_4, 3 h	0.163 ± 0.001	0.090 ± 0.001
H_3PO_4 catalyst, 1 pass	0.122 ± 0.001	0.004 ± 0.000
H_3PO_4 catalyst, 4 passes	0.111 ± 0.000	0.015 ± 0.001
H_3PO_4 catalyst, 8 passes	0.103 ± 0.001	0.024 ± 0.001

[a] The radioactivity of the starting ketone was 0.126 ± 0.001 mCi/mol. [b] The radioactivity of the starting ketone was 0.254 ± 0.002 mCi/mol. [c] Starting material isotopic purity and degradation procedure check.

extensive decomposition of the ketone. The experimental procedures for the preparation of the labeled ketone, the rearrangement, and the degradation of the recovered ketone have been described.[11,13] The degradation of the product 3-methyl-2-butanone-*X*-^{14}C involved peracid oxidation to isopropyl acetate, followed by derivatization of the acid and alcohol components of the ester to acetanilide and isopropyl 3,5-dinitrobenzoate, respectively. Thus, the activities of the acetanilide and isopropyl 3,5-dinitrobenzoate are measures of the amounts of the label in the acetyl and isopropyl groups of the ketone. The results are shown in Table II.

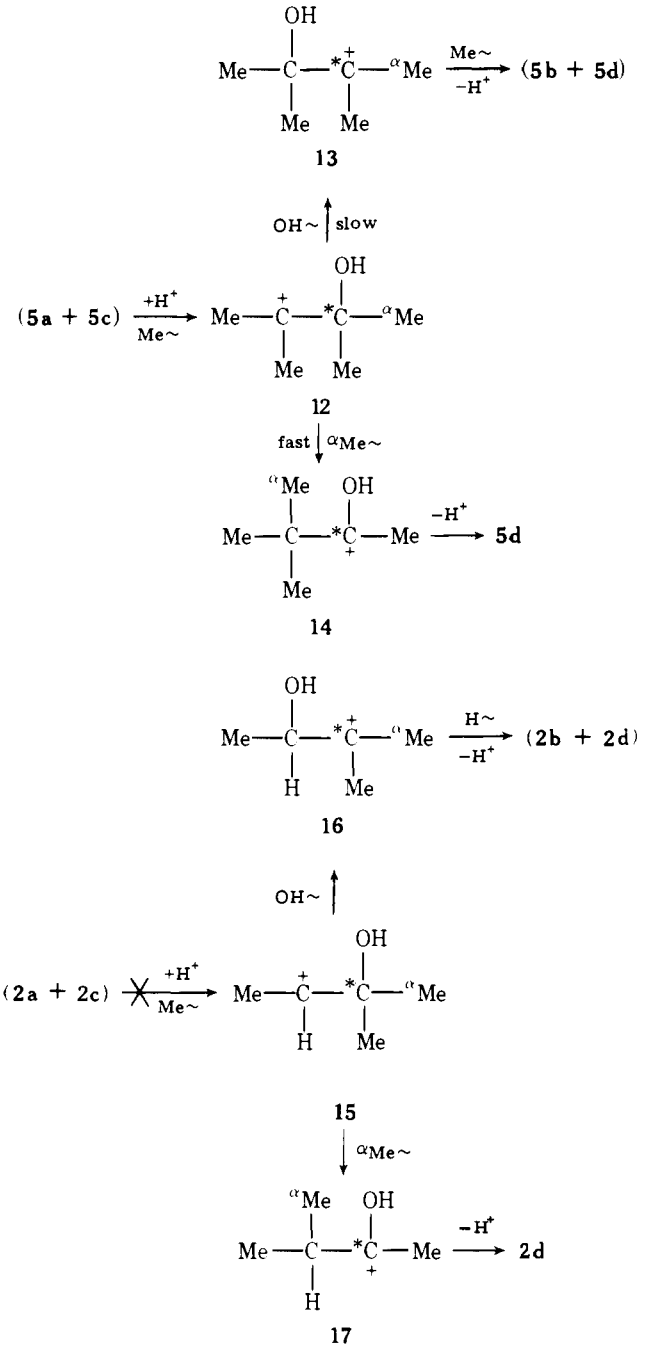
The zero time sample result shows the isotopic purity of the starting material and the adequacy of the degradation procedure. The very low activities in the isopropyl 3,5-dinitrobenzoate demonstrate that very little, if any,[17] of isomer **2b** is formed from **2a** under either set of reaction conditions. Thus, there is no oxygen function rearrangement, and the type of acid system makes no difference, both as predicted.

This result, **2a** $\not\rightleftharpoons$ **2b**, might mean that nothing at all had happened, but it seemed more likely that methyl scrambling, **2c** $\rightleftharpoons$ **2d**, would be taking place. Such methyl scrambling does take place[11,18] with 3,3-dimethyl-2-butanone, **5c** $\rightleftharpoons$ **5d**, presumably by mechanism Ia (eq 2). However, application of this mechanism to 3-methyl-2-butanone would require the intermediacy of a high-energy secondary R^+ whereas in the methyl scrambling of 3,3-dimethyl-2-butanone the intermediacy of a more stable tertiary R^+ would be required. Accordingly, the rearrangement of 3-methyl-2-butanone-1-^{14}C was studied using both the solid supported phosphoric acid and concentrated sulfuric acid catalyst systems. The results are shown in Table III.

The increase in activity in the isopropyl derivative and the decrease in activity in the acetyl derivative as time increases in the sulfuric acid case or as the number of passes over solid supported phosphoric acid increases show clearly that methyl group scrambling, **2c** $\rightleftharpoons$ **2d**, does take place, as predicted. It is to be noted that the activity balances are good in all cases.

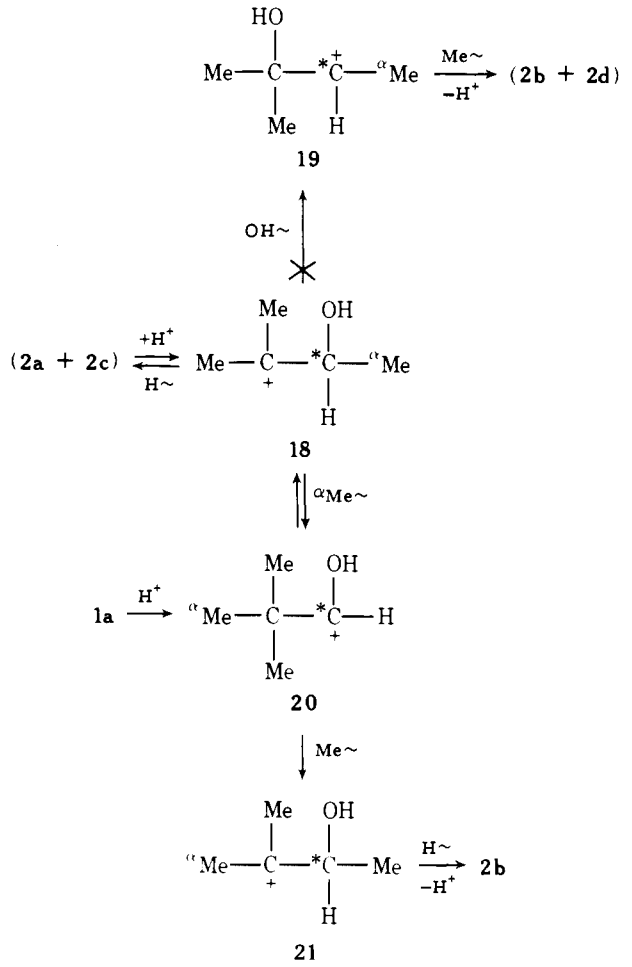
These experiments point up the unsatisfactory nature of mechanism Ia (eq 2) for rearrangements of α-monosubstituted ketones. The critical intermediates in the application of mechanism Ia in combination with mechanism IIa to the 3,3-dimethyl-2-butanone and 3-methyl-2-butanone cases are shown below.[19]

Compounds **5b** and **5d** are known[11] to be formed from **5a** and **5c**, the formation of **5d** being much faster than the for-



mation of **5b**. Tertiary carbenium ion **12** rearranges slowly to isomeric tertiary carbenium ion **13** and more rapidly to ketone conjugate acid **14**, as might be expected from cation stability orders. But, as shown above, **2a** does not rearrange to **2b**, although **2c** does form **2d**. If secondary carbenium ion **15** were actually an intermediate, its rearrangement to tertiary carbenium ion **16** should certainly be more favorable than the **12** → **13** tertiary R^+ → tertiary R^+ rearrangement. The conclusion seems inescapable that secondary carbenium ion **15** is not an intermediate.

Mechanism Ib (eq 3), although involving more steps, provides a satisfactory rationale for the observed results. As this mechanism is applied (in combination with mechanism IIa) to the 3-methyl-2-butanone case the critical intermediates are shown below.[19] By this mechanism, tertiary carbenium ion **18**



would not be expected to rearrange to secondary carbenium ion **19** and hence no **2d**, the oxygen function rearrangement product, should be formed. The preferred path from **2a** through ions **18**, **20**, and **21** to **2b** involves only tertiary carbenium ions and an aldehyde conjugate acid. The conversion of the aldehyde **1a** to the isomeric ketone **2a** is known[13] to be fast (see eq 5).

At this point the rationale for predictions 4 and 5 (Chart I) becomes clear. α-Monosubstituted ketone **8a** should follow mechanism Ib just as **2a** does, with no oxygen function rearrangement, and α-disubstituted ketone **10a** should follow mechanism Ia in combination with mechanism IIa just as compound **5a** does, with **11a** forming as the major product (mechanism Ia) and **11b** forming as the minor one (mechanism IIa).

Rearrangement of 2,4-Dimethyl-3-pentanone-*3*-^{14}C (8a). Upon treatment with concentrated sulfuric acid, 2,4-dimethyl-3-pentanone rearranges to 3,4-dimethyl-2-pentanone.[20]

Table IV. Activity Results (mCi/mol) Obtained for the Rearrangement of 2,4-Dimethyl-3-pentanone-*3*-^{14}C (**8a**) in Concentrated Sulfuric Acid for 3 h at 88 and 99 °C

compd	88 ± 1 °C	99 ± 1 °C
2,4-dimethyl-3-pentanone-*3*-^{14}C	0.0418 ± 0.0001	0.0903 ± 0.0003
2,3-dimethylbutyric-*X*-^{14}C acid *p*-toluidide	0.0412 ± 0.0002	0.0927[a] ± 0.0003
N-(1,2-dimethylpropyl)benzamide-*X*-^{14}C	0.0413 ± 0.0002	0.0926[a] ± 0.0006
benzoic-7-^{14}C acid	0.0398[b] ± 0.0002	0.0892[b] ± 0.0007
N-(1,2-dimethylpropyl-*1*-^{14}C)-benzamide	0.000 06[c] ± 0.000 01	0.000 16[c] ± 0.000 01

[a] These high values may be due to normal isotope effects—see text. [b] These low values may be due to normal isotope effects—see text. [c] Indistinguishable from the counting rate for blank samples.

Independent experiments were carried out for the rearrangement of **8a** in concentrated sulfuric acid at 88 and 99 °C. The second experiment at the higher temperature was an attempt to use the most drastic possible conditions so as to provide maximum opportunity for oxygen function rearrangement to occur. More than 70% of the material decomposed in this experiment. The mixture of recovered ketones, mostly 3,4-dimethyl-2-pentanone-*X*-^{14}C (possibly a mixture of **9a** and **9b**), with a small amount of residual **8a**, was subjected to a haloform reaction. Ketone **8a** did not react and was subsequently separated by extraction from basic solution from the main reaction product, 2,3-dimethylbutyric-*X*-^{14}C acid. This acid was degraded by the method used[21] for cyclopropanecarboxylic-*X*-^{14}C acid. The isocyanate formed from the acid by the Curtius reaction was converted to *N*-(1,2-dimethylpropyl)benzamide-*X*-^{14}C by reaction with phenylmagnesium bromide. Hydrolysis of the amide gave benzoic-7-^{14}C acid and 1,2-dimethylpropyl-*1*-^{14}C-amine, which was further derivatized to *N*-(1,2-dimethylpropyl-*1*-^{14}C)benzamide. The activity of the benzoic-7-^{14}C acid is thus a measure of the amount of **9a** and that of the *N*-(1,2-dimethylpropyl-*1*-^{14}C)benzamide is a measure of the amount of **9b** (the amount of oxygen function rearrangement) in the 3,4-dimethyl-2-pentanone-*X*-^{14}C. The results are shown in Table IV.

The activity of the final *N*-(1,2-dimethylpropyl-*1*-^{14}C)-benzamide samples from both experiments was at the background level, showing that none of isomer **9b** had been formed (and also confirming the radioactive purity of the **8a**). The prediction that there would be no oxygen function rearrangement in this reaction was borne out, giving strong support to the thesis that α-monosubstituted ketones rearrange by mechanism Ib.

In the 99 °C experiment the activities of the derivatives of the recovered ketone are about 2.5% higher than that of the starting ketone. All things considered, this is not a serious problem, but it is interesting to speculate that this enhancement of activity may arise from normal isotope effects in the extensive decomposition and polymerization reactions (more than 70%) which accompany the rearrangement at the higher temperature. If the decomposition and polymerization reactions involve bonding changes at the carbonyl carbon of **8a**, the unlabeled molecules should react faster leading to enrichment of the carbon-14 in the residual ketone, as observed. This decomposition problem was not so severe in the 88 °C experiment.

In the experiments at both temperatures the benzoic-7-^{14}C activity was about 2% lower than the amide from which it was formed by hydrolysis (and no activity was found in the amine

hydrolysis product). Again, this is not a serious problem, but it was known that the hydrolysis was not quantitative and this lower activity value for the benzoic acid is exactly what would be expected if there were an isotope effect for such an incomplete hydrolysis reaction.[22] As confirmation of this isotope effect thesis, the residual *N*-(1,2-dimethylpropyl)benzamide-*X*-^{14}C samples from the hydrolyses were recovered and found to have increased activities, 0.0431 ± 0.0002 and 0.0946 ± 0.0005 mCi/mol, as expected.[23]

Rearrangement of 2,2,4-Trimethyl-3-pentanone-3-^{13}C (10a). α-Disubstituted ketone **10a,** upon treatment with concentrated sulfuric acid, has been shown to rearrange to **11a** as the major product (~93%) and **11b** as the minor product (~7%). Details of the tracer study are reported elsewhere.[16] This result is that predicted in Chart **I**, rearrangement to form the major product by mechanism Ia, and to form the minor product by mechanism IIa.

The rearrangement of ketone **10a** also provides insight into two other important mechanistic questions: reversibility of the oxygen function rearrangement and the relative importance of mechanisms Ia and Ib in cases where both might be important.

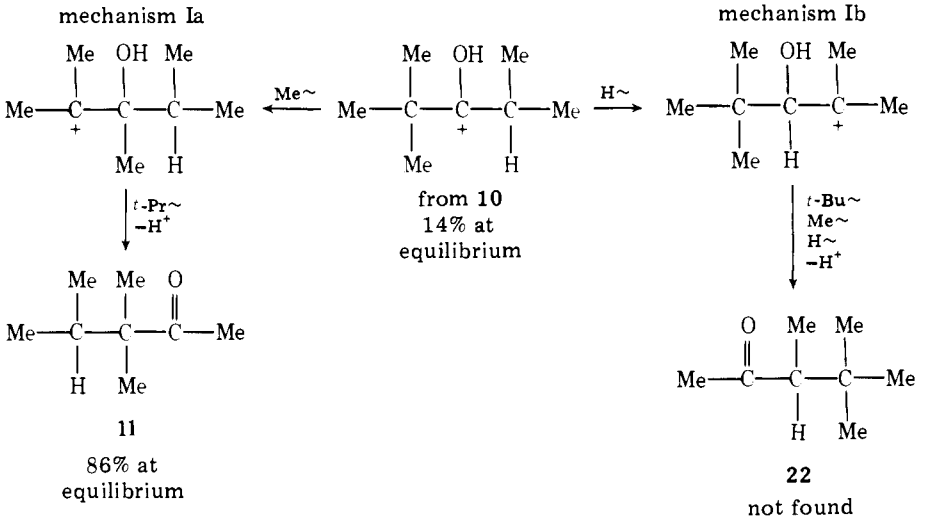
In all the mechanisms proposed for ketone rearrangements, reversibility is a key feature, and this has been demonstrated many times. Equilibrium constants have been determined in many cases.[7,10,11,16,18,25,26] However, the reversibility of the oxygen function rearrangement had not been directly demonstrated until the work on ketone **10a.**[16,27] When **10a** is heated with sulfuric acid, the equilibrium mixture consists of ~86% of **11** and ~14% of **10.** The isotopic composition of the recovered ketone **10** was shown[16] to be ~94% **10a** and ~6% **10b,** 2,2,4-trimethyl-3-pentanone-2-^{13}C. Even in this case, **10b** might have come from oxygen function rearrangement product **11b** via mechanism Ia rather than via a direct reversal of the step in which the oxygen function changes carbons.

Application of mechanisms Ia and Ib to 2,2,4-trimethyl-3-pentanone (**10**) leads to different products: 3,3,4-trimethyl-2-pentanone (**11**) from mechanism Ia, and 3,4,4-trimethyl-2-pentanone (**22**) from mechanism Ib. In both mechanisms, only similar tertiary carbenium ions and aldehyde or ketone conjugate acids are intermediates. This reaction provides a clear demonstration of the much greater migratory aptitude of methyl than of hydrogen in these ketone rearrangements.[28]

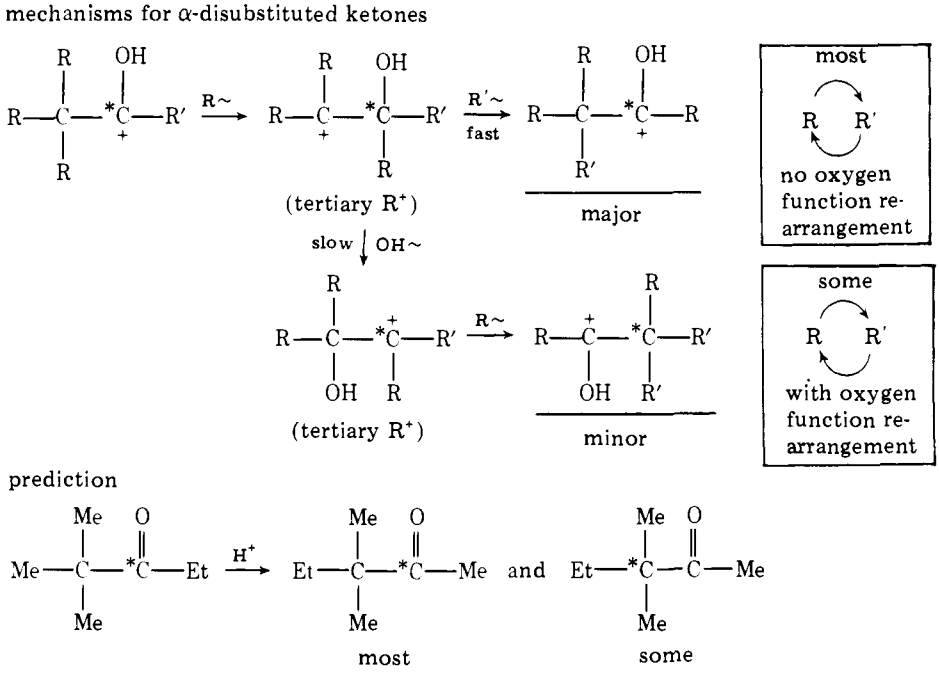
In the reaction of **10** with concentrated sulfuric acid at 70 °C for 2 h, GLC analysis of the recovered reaction mixture showed the presence of only two compounds, **10** (14%) and **11** (86%), with no low-boiling decomposition products. Despite a careful search, no trace of **22** could be found (estimated detection limit, 0.1%). The same equilibrium mixture of **10** and **11** was obtained under the same conditions, starting with **11.** The equilibrium constant for **10** ⇄ **11** is 6.2 ± 0.3, in agreement with that reported[25] by Zook, Smith, and Greene. Ketone **11** was isolated by preparative GLC and identified by 60- and 90-MHz ^1H NMR, with appropriate decoupling experiments, δ 0.79 (d, 6 H, J = 6.8 Hz), 0.96 (s, 6 H), 1.95 (septet, 1 H, J = 6.8 Hz), 1.97 (s, 3 H). Ketone **11** had earlier been identified[15,25] as the primary product of this reaction by infrared techniques. Even at higher temperatures, where substantial decomposition took place, no conclusive evidence for compound **22** could be found, although one of the low-yield decomposition products may have been butanone from a cleavage reaction of **22.** These cleavage reactions have been known for a long time,[25] and have been studied intensively in more recent years.[29] They are a serious complication in any study of highly branched ketones in strong acid solution.

This preference for methyl over hydrogen migration, and other aspects of the kinetics of ketone rearrangements, has been studied extensively by Brouwer and Van Doorn.[7] For instance, they showed that the relative rates of acid-catalyzed rearrangement of 2,2-dimethyl-3-pentanone (rate-determining methyl migration, mechanism Ia) and 2-methyl-3-pentanone (rate-determining hydrogen migration, mechanism Ib) are about 100:1. A similar comparison is available from the present work. From the data in Table II it is possible to make a rough calculation by the method used before[11] of the rate constant for methyl scrambling in concentrated sulfuric acid at 100 °C (**2c** → **2d**) in 3-methyl-2-butanone (hydrogen migration, mechanism Ib), 4.8 × 10^{-5} s^{-1}, compared to that calculated[11,30] for methyl scrambling (**5c** → **5d**) in 3,3-dimethyl-2-butanone (methyl migration, mechanisms Ia and IIa), 54 × 10^{-5} s^{-1}.

Other aspects of the kinetics work of Brouwer and Van Doorn[7] are pertinent to the present mechanistic discussion. Mechanism Ib involves the intermediacy of an aldehyde conjugate acid. Despite exhaustive searches, no aldehydes have ever been found in ketone to ketone rearrangements. Brouwer and Van Doorn showed that the relative rates of rearrangement at 25 °C are approximately 10^7:10^2:10^2:1 for (1) α-dibranched aldehydes to α-monobranched ketones; (2) α-monobranched aldehydes to α-unbranched ketones; (3) α-dibranched ketones; (4) α-monobranched ketones. Also, it is known[10] that rearrangements of α-unbranched ketones take place very much slower than any of the above. Clearly then, if aldehyde conjugate acids were intermediates in ketone rearrangements, they would be extremely reactive toward further rearrangement, and would not be found as isolatable products. Nevertheless, there are compelling mechanistic arguments for the inter-



Scheme I



mediacy of aldehyde conjugate acids in the rearrangements of α-monosubstituted ketones (see the discussion of the rearrangement of **2a** and **2c** above).

Mechanistic Conclusions. Paths of Acid-Catalyzed Ketone Rearrangements

Based on all of the available evidence, and especially on the results of the critical experiments described above, the mechanisms for the acid-catalyzed rearrangements of aliphatic ketones may be divided into three related classes, depending on the degree of substitution of the most substituted carbon α to the carbonyl group. The key data on which the mechanistic classification is based come from studies of the relation of structure to the presence or absence of oxygen function rearrangement, and from relative rate studies.

In all cases studied, the particular nature of the acid catalyst, which sometimes drastically changes rates and amounts of side reactions, appears to result in no qualtitative changes in mechanism.

The predictive power of two of the three mechanistic schemes presented below has been demonstrated by the experiments described above. Only in the case of the α-unsubstituted ketones does there still appear to be substantial mechanistic uncertainty. These mechanistic schemes integrate, as appropriate, the various partial mechanisms used previously in this paper. In all cases the starting and product ketones are shown as their conjugate acids. The intermediates, except as noted, are all presented as open carbenium ions[6] (primary, secondary, or tertiary R^+) or aldehyde conjugate acids. The oxygen function rearrangements in Schemes I and II are shown as OH migrations, but in most studied cases other oxygen function rearrangement mechanisms have not been excluded (see the mechanism IIa discussion above and ref 3). The observed product conjugate acids are underlined and the favored mechanistic paths are indicated by the boxes. Some alternate mechanistic pathways are shown, with the points at which they are blocked indicated. All of the allowed reactions are considered to be reversible. In each of the three cases a prediction is made for a specific case for which full experimental data are not available. As is already well known,[3] methyl ketones are always favored under equilibrating conditions.

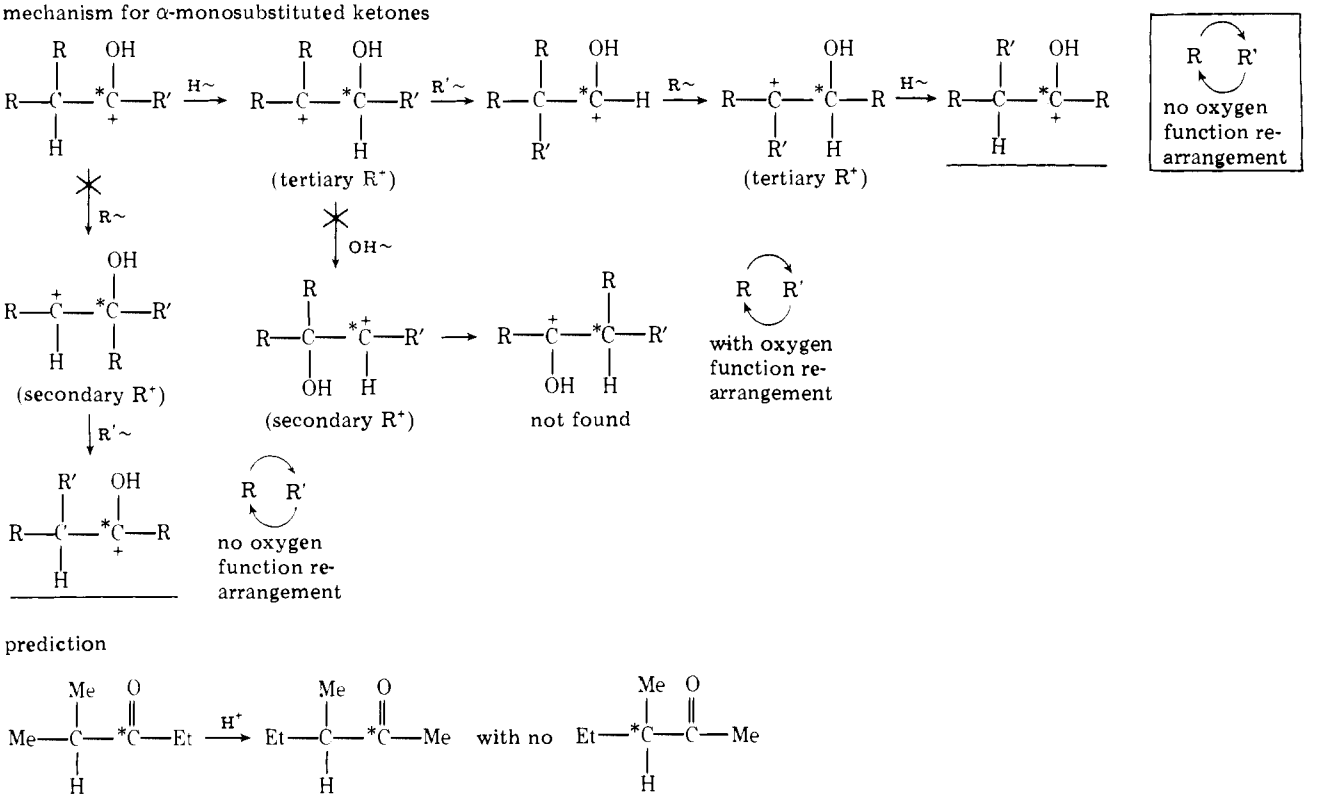
Mechanisms for α-Disubstituted Ketones. For α-disubstituted ketones, Scheme I, the favored mechanistic path involves fast interchange of a group attached directly to the carbonyl carbon with a group attached to the α carbon on the other side of the carbonyl group (R,R′ interchange), accompanied by slower oxygen function rearrangement. The choice between simple R,R′ interchange and oxygen function rearrangement is made in the further reaction of the tertiary R^+ formed by the first alkyl group migration. The preference for simple R,R′ interchange over oxygen function rearrangement reflects the greater stability of the ketone conjugate acid so formed compared to the isomeric tertiary R^+ formed by OH migration. The finding of the predicted results with ketone **10a** described above strongly supports this mechanistic pattern. These α-disubstituted ketones are very prone to cleavage reactions.[29] In the "prediction", the chemical result is known,[31] but the oxygen function rearrangement result is not.

Mechanism for α-Monosubstituted Ketones. Scheme II shows the preferred path for the rearrangements of α-monosubstituted ketones. These reactions are much slower than the rearrangements of α-disubstituted ketones. This route involves only tertiary R^+ and aldehyde conjugate acids, in contrast to alternate paths involving higher energy secondary R^+. The comparative results with the **2a, 2c** and **5a, 5c** systems, and the finding of the predicted results with ketone **8a** described above, show that reaction via the shorter route involving a secondary R^+ is highly unlikely. In the "prediction", the chemical result is known,[10] but the oxygen function rearrangement result is not.

Mechanism for α-Unsubstituted Ketones. α-Unsubstituted ketones rearrange only very slowly under very drastic conditions, and then always with many side reactions and much decomposition.[3,10,14,20,32,33] Only one oxygen function rearrangement study has been carried out[14] on an all-aliphatic system, **3a** → **4b** (eq 6). For these reasons the mechanism in Scheme III must be considered to be speculative. Since **3a** forms **4b** and no appreciable **4a** (see eq 6), the route leading to **4a** through the primary R^+ (top path) is unacceptable. The horizontal route through a secondary R^+ would give the correct product, **4b**, but the first secondary R^+ in that path would surely be expected to rearrange (vertical arrow) to an aldehyde conjugate acid (leading, eventually to the incorrect product) in preference to an isomeric secondary R^+ (dashed X). Thus, rearrangement to an open secondary R^+ is not likely. The favored alternative involves (left-hand vertical path) concerted

Scheme II

mechanism for α-monosubstituted ketones



prediction

formation and subsequent decomposition of an epoxide conjugate acid. Of the various acid catalysts tried, only the solid supported phosphoric acid system[10] offers much hope of extensive rearrangement without too excessive an amount of decomposition for these α-unsubstituted ketones. Again, in the "prediction", the chemical result is known,[10] but the oxygen function rearrangement result is not.

Experimental Section

General. The radioactivity measurements reported in Tables I-IV were determined on a Beckman LS 100 liquid scintillation system using a cocktail solution prepared from 5 g of PPO (2,5-diphenyloxazole), 0.2 g of DMPOPOP (1,4-bis[2-(4-methyl-5-phenyloxazole)]-benzene), and 1 L of toluene, using the external standard ratio method. A quench calibration curve for the external standard ratio method was prepared by using samples of benzoic-7-^{14}C acid for which the radioactivity level had already been determined and by using chloroform as a quenching agent.[34] All samples were recrystallized to constant activity before the reported radioactivity measurements were made. The activities reported are averages of at least three determinations for the same sample. The activities of all ketones reported were determined on the semicarbazone derivatives unless otherwise noted. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The melting points for all derivatives and degradation products obtained in the reactions described below always agreed with these reported values: 3-methyl-2-butanone semicarbazone, mp 113-114 °C, reported[35] mp 114 °C; 3,3-dimethyl-2-butanone semicarbazone, mp 155-156 °C, reported[36] mp 157 °C; 2,4-dimethyl-3-pentanone semicarbazone, mp 158-160 °C, reported[37] mp 160 °C; acetanilide, mp 113-114 °C, reported[38] mp 114 °C; isopropyl 3,5-dinitrobenzoate, mp 121-122 °C, reported[39] mp 122 °C; *tert*-butyl 3,5-dinitrobenzoate, mp 140-141 °C, reported[39] mp 142 °C; 2,3-dimethylbutyric acid *p*-toluidide, mp 112 °C, reported[40] mp 112.6 °C; *N*-(1,2-dimethylpropyl)benzamide, mp 71-73 °C; benzoic acid, mp 121-122 °C, reported[41] mp 122 °C. All spectra were taken on standard commercial instruments.

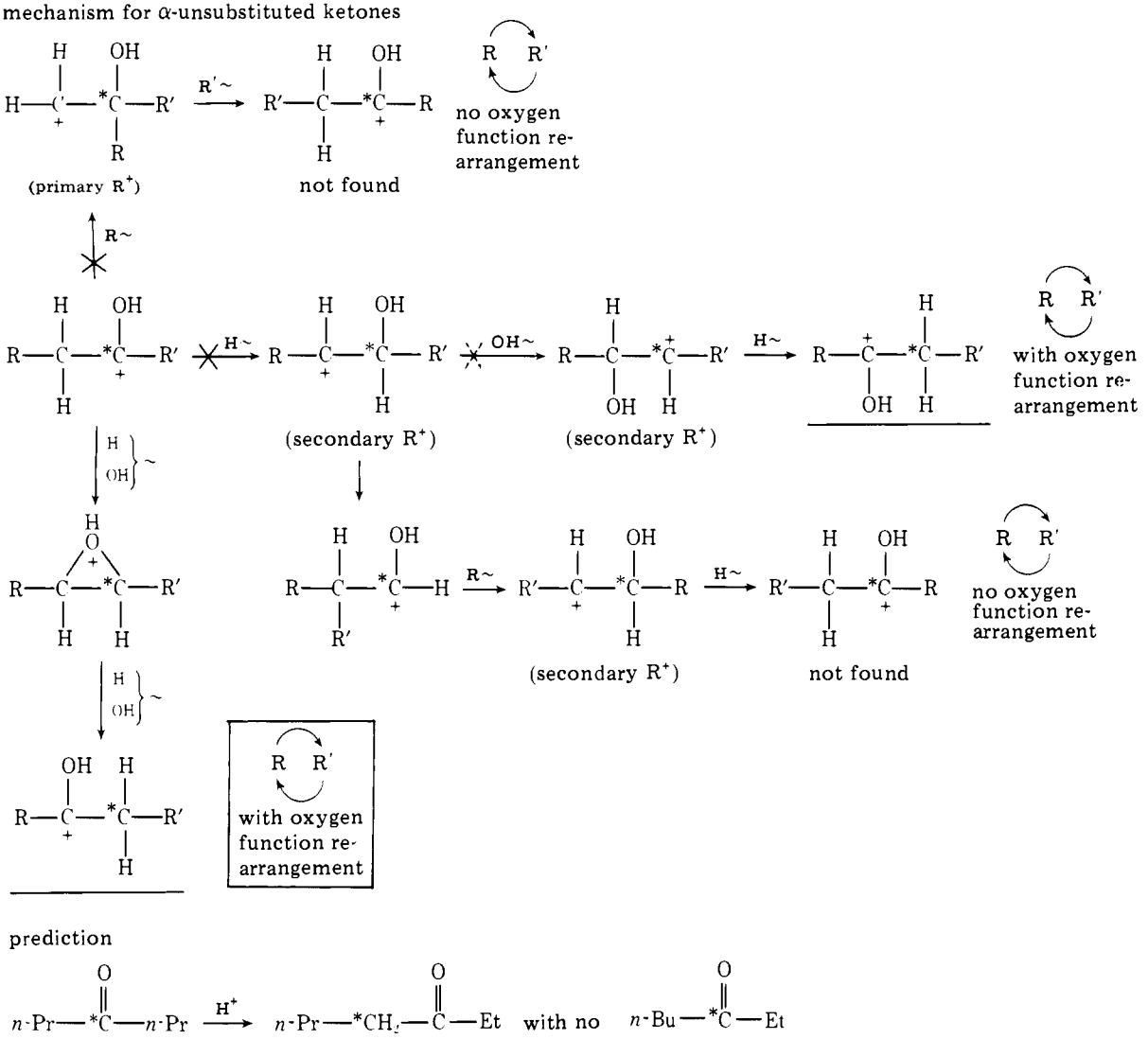
3-Methyl-2-butanone-2-^{14}C (2a). Compound **2a** was prepared by rearrangement of trimethylacetaldehyde-1-^{14}C (**1a**) over solid supported phosphoric acid catalyst at 230 °C as previously described.[13] After passage through the catalyst column, the ketone recovered was washed with a small portion of water, dried over sodium sulfate, and then distilled, bp 93 °C, reported[35] bp 93-94 °C. In a typical experiment, the yield was 80%. Analysis of the labeled ketone by GLC and NMR showed that the ketone obtained was chemically very pure, >99.5%. The radiochemical purity of the labeled ketone was established as excellent by the degradation procedure (see Table II).

3-Methyl-2-butanone-1-^{14}C (2c). Compound **2c** was prepared by the procedure of Newman and co-workers[42] by adding methylmagnesium-^{14}C iodide from 14.2 g (ca. 0.5 mCi, Research Specialties Co.) of methyl-^{14}C iodide and 2.7 g of magnesium in 50 mL of ether to 31.7 g of isobutyric anhydride in 125 mL of ether over a 75-min period at a temperature of −70 to −80 °C. The mixture was stirred for an additional 1 h and worked up with ammonium chloride solution. After extracting with ether, washing with sodium hydroxide solution, and drying, distillation gave 5.2 g (60%) of **2c**, bp 93 °C (740 mm), reported[35] bp 94 °C. Analysis by GLC and NMR showed the chemical purity to be >99.5%. This material was diluted with inactive 3-methyl-2-butanone as needed. The radiochemical purity was established as excellent by the degradation procedure (see Table III).

3,3-Dimethyl-2-butanone-2-^{14}C (5a). Compound **5a** was available from previous work.[11] The high chemical purity of the compound was established by GLC and NMR analysis. The radiochemical purity was established as excellent by the degradation procedure (see Table I).

2,4-Dimethyl-3-pentanone-3-^{14}C (8a). Sodium isobutyrate-1-^{14}C (Amersham/Searle, 0.1 mCi, ca. 1.5 mg) was refluxed with 10.7 g of unlabeled isobutyryl chloride for 6 h. The entire reaction mixture of isobutyryl-1-^{14}C chloride and ~1.5 mg of exchanged salt was placed in a 250-mL three-neck flask equipped with a condenser, mechanical stirrer, and dropping funnel, and 11.0 g of cuprous chloride and 60 mL of ether were added. The suspension was stirred for 10 min at 0 °C and then isopropylmagnesium bromide prepared from 13.5 g of isopropyl bromide and 2.94 g of magnesium in 50 mL of ether was added at 0 °C over a 30-min period. Stirring was continued for an additional 25 min, and the mixture was worked up in the usual way, including a sodium hydroxide wash. Distillation gave 7.70 g (67%) of **8a**, bp 122 °C (738 mm), reported[37] bp 124-125 °C. Analysis by GLC and NMR showed the chemical purity to be very high, >99.8%. The radiochemical purity was checked by comparing the activity of the liquid ketone (0.97 mCi/mol) to that of its recrystallized semi-

Scheme III



carbazone (0.95 mCi/mol). Radiochemical purity from other isotopic isomers is demonstrated by the lack of activity in the noncarbonyl part of the molecule in the degradation of the ketone recovered from the rearrangement experiments (see Table IV). The labeled ketone was diluted with unlabeled 2,4-dimethyl-3-pentanone as needed.

Rearrangement of 3,3-Dimethyl-2-butanone-*2*-^{14}C (5a) over Solid Supported Phosphoric Acid at 225 °C. The experimental procedure used was that described previously.[13] A sample of 30 mL of **5a** was passed six times through a solid supported phosphoric acid catalyst column at 225 °C. Samples were removed after each pass for GLC analysis and after passes 1, 3, 5, and 6 for degradation (the entire sample remaining after pass 6 was used for degradation). The samples analyzed after passes 5 and 6 showed trace amounts of low boiling point decomposed materials

Degradation of 3,3-Dimethyl-2-butanone-*X*-^{14}C. The procedure used was similar to that previously described.[11] The ~5-mL samples of recovered ketone were mixed with 17.5 g of *m*-chloroperbenzoic acid in 300 mL of methylene chloride. The reaction mixture was allowed to stand for 4 days at 32 °C, and then worked up in the usual way. Distillation of the methylene chloride solution gave about 5 mL of *tert*-butyl acetate, bp 94 °C (730 mm), reported[43] bp 98 °C. Analysis of the *tert*-butyl acetate obtained by GLC and NMR showed that the ester was very pure and identical with an authentic sample. Despite a careful search, no methyl trimethylacetate could be detected. The two derivatives, acetanilide and *tert*-butyl 3,5-dinitrobenzoate, were prepared from this ester for carbon-14 analysis. The preparation of acetanilide was the same as that previously mentioned.[13] The direct transesterification reaction[44] for the preparation of *tert*-butyl 3,5-dinitrobenzoate could not be used since *tert*-butyl acetate decomposes with a catalytic amount of strong acid. Instead, 2 mL of *tert*-butyl acetate was hydrolyzed by refluxing for 18 h using 2 g of barium hydroxide and about 5 mL of water. At the end of the reaction, the *tert*-butyl alcohol obtained was extracted by shaking with methylene chloride several times. The combined methylene chloride extracts were washed with a small amount of water and dried over sodium sulfate. After the methylene chloride was distilled, the residue was cooled, 1.5 g of 3,5-dinitrobenzoyl chloride was added, and the reaction mixture was heated gently to form *tert*-butyl 3,5-dinitrobenzoate. The crude product was washed with water and dilute sodium carbonate solution, and then recrystallized from ethanol-water to give the pure *tert*-butyl 3,5-dinitrobenzoate. The results of the degradations are shown in Table I.

Rearrangements of 3-Methyl-2-butanone-*2*-^{14}C (2a) and 3-Methyl-2-butanone-*1*-^{14}C (2c) in Concentrated Sulfuric Acid at 100 °C. In a typical experiment, 23 mL of concentrated sulfuric acid was placed in a one-neck flask, and 10 mL of 3-methyl-2-butanone-*2*-^{14}C was gradually added to the acid. The reaction mixture was shaken carefully, resulting in a light red, homogeneous solution, which was placed in an oil bath at 100 ± 1 °C for 3 h. At the end of this time, the dark-colored reaction mixture was cooled and worked up with ice-water and 8 N sodium hydroxide solution. The ketone was extracted with methylene chloride several times and the methylene chloride solution was washed with water, decolorized with charcoal, dried over sodium sulfate, and distilled. Distillation gave 5.2 mL (52% recovery) of 3-methyl-2-butanone-*X*-^{14}C, bp 93 °C, reported[35] bp 93–94 °C. The labeled ketone was degraded as before[13] to acetanilide and isopropyl 3,5-dinitrobenzoate for radioactive assay. The results of the degradations of the compounds from **2a** and **2c** are given in Tables II and III, respectively.

Rearrangements of 3-Methyl-2-butanone-*2*-^{14}C (2a) and 3-

Methyl-2-butanone-*1*-^{14}C (2c) over Solid Supported Phosphoric Acid. The experimental procedures for the rearrangement and degradation were the same as those used previously.[13] As determined by preliminary experiments on the unlabeled ketone, a temperature of 290 °C was the highest temperature (and hence the most likely to give oxygen function rearrangement with **2a**) that could be used without extensive decomposition. A sample of 26 mL of **2a** was passed four times through a solid supported phosphoric acid catalyst column at 290 °C and 5-mL degradation samples were taken after one, three, and four passes, the latter being the the entire sample remaining. Analysis by GLC showed several percent of low-boiling decomposition products in fractions 3 and 4. These impurities were removed during the workup and degradation steps. For the rearrangement of **2c**, a 25-mL sample of the ketone was passed through a solid supported phosphoric acid catalyst column at 225 °C, and 5-mL degradation samples were taken after one, four, and eight passes. The results for compounds **2a** and **2c** are shown in Tables II and III, respectively.

Rearrangement of 2,4-Dimethyl-3-pentanone-*3*-^{14}C (8a) in Concentrated Sulfuric Acid at 88 and 99 °C. In preliminary experiments to find the best conditions for the tracer studies, the rearrangement of 2,4-dimethyl-3-pentanone was carried out for 3 h at different reaction temperatures in concentrated sulfuric acid (ketone–acid ratio 1:2.3 v/v). The following results were obtained: 55% of recovered ketonic materials with 80% of the rearranged product at 88 ± 1 °C; 35% of recovered ketonic materials with 90% of the rearranged product at 95 ± 1 °C; 30% of recovered ketonic materials with 95% of the rearranged product at 100 ± 1 °C; nearly complete decomposition at 115 ± 1 °C. In order to provide the most stringent test for whether oxygen function rearrangement would take place, as drastic reaction conditions as possible were selected, and rearrangement reactions were carried out at both 88 and 99 °C. The experimental procedure used for **8a** was essentially the same as that described above for **2a** and **2c**. In the 88 °C experiment, from 7.9 g of **8a**, 4.4 g of ketonic products boiling at ~120 °C (730 mm) was recovered. Analysis by GLC and NMR showed that the distilled product was a mixture of two isomeric ketones, **8a** and its rearrangement product, 3,4-dimethyl-2-pentanone-*X*-^{14}C, in the ratio of approximately 20:80. The rearranged ketone was identified by comparison of GLC retention times and semicarbazone melting point with those of an authentic sample.[20] A sample of the rearranged ketone which was separated by preparative GLC had a ^1H NMR spectrum that was identical with the reported spectrum:[45,46] δ 0.83 (d, J = 6.0 Hz, 3 H, $(CH_3)_2CH$), 0.89 (d, J = 6.5 Hz, 3 H, $(CH_3)_2CH$), 0.98 (d, J = 6.5 Hz, 3 H, α-CH_3), 1.5–2.6 (m, 2 H), 2.02 (s, 3 H, $COCH_3$).

In order to recover about the same amount (ca. 5 mL) of the ketonic product (because of the extensive decomposition at the higher temperature) in the 99 °C experiment, 15 mL of 2,4-dimethyl-3-pentanone-*3*-^{14}C was used with 35 mL of concentrated sulfuric acid. This gave 3.87 g of a mixture of 3,4-dimethyl-2-pentanone-*X*-^{14}C (95%) and 2,4-dimethyl-3-pentanone-*3*-^{14}C (5%) with a trace amount of impurities.

Degradation of 3,4-Dimethyl-2-pentanone-*X*-^{14}C and Separation of 2,4-Dimethyl-3-pentanone-*3*-^{14}C. A mixture of the two isomeric ketones was subjected to a haloform reaction to give the corresponding acid, 3,4-dimethyl-2-butyric-*X*-^{14}C acid, and unreacted 2,4-dimethyl-2-pentanone-*3*-^{14}C. A solution of 14.20 g of sodium hydroxide in 120 mL of water in a 250-mL bottle was prepared, and 6.7 mL of bromine was added carefully at temperatures below 10 °C. A mixture of 4.38 g of the two ketones was then added. The reaction mixture was stirred vigorously for 3.0 h at 0 °C. There was no appreciable amount of 3,4-dimethyl-2-pentanone-*X*-^{14}C left after 3 h as shown by GLC analysis. At the end of the reaction, 13 mL of 20% sodium bisulfite solution was added to the reaction mixture to destroy excess hypobromite, and the organic layer which formed (bottom) was separated from the aqueous layer. The ^1H NMR spectrum of this organic phase showed the presence of bromoform and 2,4-dimethyl-3-pentanone. The aqueous solution from the haloform reaction was extracted with ether four times to remove neutral materials and acidified with 9 mL of concentrated sulfuric acid to liberate the organic acid, 2,3-dimethylbutyric-*X*-^{14}C acid. The acid was extracted into ether, washed with water, dried over calcium chloride, and distilled to yield 2.80 g (79%) of the acid, bp 187 °C (726 mm), reported[40] bp 189–191 °C. The IR, NMR, and mass spectra and the melting point of the *p*-toluidide of the acid obtained from the bromoform reaction on a sample of unlabeled ketone were identical with those of an authentic sample. The labeled acid (0.3 g) was used to prepare the *p*-toluidide by standard methods for ^{14}C assay of the 2,3-dimethylbutyric-*X*-^{14}C acid.

Degradation of 2,3-Dimethylbutyric-*X*-^{14}C Acid. The experimental procedure used was similar to that reported[21] for degradation of cyclopropanecarboxylic-*X*-^{14}C acid. A mixture of 1.62 g of 2,3-dimethylbutyric-*X*-^{14}C acid and 1.95 g of thionyl chloride in a 25-mL flask was refluxed for 70 min, cooled in an ice–water bath, and poured into a 100-mL flask containing 23 mL of cold tetrahydrofuran. A cold solution prepared from 4.88 g of sodium azide in 23 mL of water was added, and the reaction mixture was vigorously stirred for 5 min in an ice–water bath and then for 30 min at room temperature. The mixture was poured into 75 mL of cold saturated sodium chloride solution, followed by extraction with toluene five times. The combined extract was washed with water, dried over magnesium sulfate, then over Drierite, and heated at reflux for 2.5 h. The solution was cooled and added during 20 min to a solution of phenylmagnesium bromide prepared from 9.42 g of phenyl bromide, 1.50 g of magnesium, and 75 mL of ether, and the reaction mixture was refluxed for 45 min. After being cooled, the reaction mixture was worked up with 60 mL of 10% hydrochloric acid. The ether layer was separated and the aqueous layer was extracted with ether twice. The combined ether extract was washed with water three times and the solvents were distilled. After most of the toluene was distilled, 75 mL of water was added to effect an azeotropic steam distillation of the rest of the toluene and the biphenyl formed as a side product when the Grignard reagent was prepared. The crude *N*-(1,2-dimethylpropyl)benzamide-*X*-^{14}C obtained was partially purified by recrystallization from ethanol–water with charcoal to give about 2 g of a crude product which was sublimed to give 1.90 g (71.3%) of the pure *N*-(1,2-dimethylpropyl)benzamide-*X*-^{14}C. A portion of this material was used for carbon-14 analysis. The NMR, IR, and mass spectra and the melting point of the *N*-(1,2-dimethylpropyl)benzamide prepared in this manner from unlabeled 2,3-dimethylbutyric acid were identical with those of an authentic sample prepared from benzoyl chloride and 3-methyl-2-aminobutane.

Hydrolysis of *N*-(1,2-Dimethylpropyl)benzamide-*X*-^{14}C. The purified *N*-(1,2-dimethylpropyl)benzamide-*X*-^{14}C (0.8 g) was mixed with 9 mL of water and 9 mL of concentrated sulfuric acid in a 25-mL flask, and the reaction mixture was gently refluxed for about 30 h. At the end of the reaction, a considerable amount of insoluble white solid (benzoic acid) was observed. The very dark reaction mixture was cooled and filtered to separate the crude benzoic acid, and the liquor was saved for the preparation of the amine derivative. The benzoic acid was washed with a small amount of water and dissolved with 20% sodium hydroxide solution. The basic solution was extracted with ether three times, cooled in an ice–water bath, and acidified with 30% sulfuric acid to regenerate benzoic acid. After being filtered, the benzoic acid was washed with water and recrystallized from water to give a product of mp 121–122 °C, reported[41] mp 122 °C. This benzoic-7-^{14}C acid was assayed for its carbon-14 activity.

The mother liquid saved from the amide hydrolysis was diluted with water, and the unreacted starting material and decomposed material were extracted with ether four times. The solution was heated to evaporate the ether and cooled again, and 10 N sodium hydroxide solution was added to make a basic solution. Into this solution was added 0.8 mL of benzoyl chloride and the reaction mixture was vigorously stirred at room temperature for 2.5 h. The *N*-(1,2-dimethylpropyl-*1*-^{14}C)benzamide obtained was separated, recrystallized from ethanol–water, and sublimed to give a product of mp 72 °C, authentic sample mp 72.5–73.5 °C. The carbon-14 activity of this material was determined.

The results of the radioactivity measurements for these experiments are shown in Table IV.

References and Notes

(1) Part 5 in the series Reactions of Ketones and Related Compounds with Solid Supported Phosphoric Acid Catalyst. See ref 13 for part 4. Supported by U.S. Atomic Energy Commission Contract AT-(40-1)-3234 and National Science Foundation Grant CHE 76-09809; taken, in part, from the Ph.D. Dissertation of M.O., University of Arkansas, 1973; presented in part, at the First Rocky Mountain Regional Meeting of the American Chemical Society, Fort Collins, Colo., June 30–July 1, 1972.

(2) M.O. would like to thank California State Polytechnic University, Pomona, for providing him with facilities to complete this manuscript.

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Photodissociation Spectroscopy of Alkane Radical Cations

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Abstract: Photodissociation spectra are reported for gas-phase radical cations of straight-chain and cyclic alkanes C_5 to C_8 (along with *n*-butane). Large photodissociation cross sections, in the neighborhood of 10^{-17} cm^2, are observed for these ions. The spectrum of cyclopentane ion suggests ring opening to give a pentene ion structure, but the other cycloalkane ions appear to retain a saturated hydrocarbon structure. The *n*-alkane ion spectra are compared with photoelectron spectra of the neutrals and do not correspond very closely. Calculations of the predicted optical spectra of the ions are made by using a conformationally averaged MINDO/3 approach with the inclusion of transition moment weighting, and the correspondence of theory and experiment is encouraging. The long-wavelength portions of the spectra of hexane and octane ions are unexpectedly weak, and some influence by threshold truncation effects is suggested.

Introduction

It was first reported in 1976[1] that the gas-phase radical cations of saturated hydrocarbons have strong optical absorptions in the visible region of the spectrum. The strongly colored nature of the alkane radical ions is in striking (through not unpredictable) contrast to the neutral alkanes, and study of the optical spectroscopy of these ions using photodissociation spectroscopic techniques has continued.[2,3] We report here a set of photodissociation spectra for the series of linear and cyclic alkanes from C_5 to C_8 (as well as *n*-butane) and give more quantitative theoretical attention to the features of these spectra than has been reported previously.

Experimental Section

The photodissociation spectra were collected by two variations of the ion cyclotron resonance (ICR) photodissociation technique. Some spectra were obtained by the steady-state method described previously.[4,5] Ions are continuously formed by electron impact until the ion population reaches a steady-state level. Photodissociation is monitored by measuring the decrease in the steady-state level upon irradiation. The steady-state method was found to be extremely difficult for alkane ions because the parent ions are highly reactive. Many of the primary ionization fragments, photofragments, and ion-molecule reaction products are much less reactive than the parent radical

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